STANDARD OPERATING PROCEDURE

Determination of Total Metals in Sediments by Inductively Coupled Argon Plasma (ICAP) Atomic Emission Spectroscopy

CRL METHOD #MET413

1. SCOPE AND APPLICATION

1.1 This procedure is applicable to the determination of sediments, sludges, and other certain solids for the following metals: aluminum, barium, boron, calcium, cadmium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, potassium, silver, sodium, strontium, tin, vanadium, yttrium, and zinc. The detection limits and concentration ranges are given in Table 1. This method is not applicable to paints, very oily sludges, and other samples of highly organic nature.

2. SUMMARY OF METHOD

2.1 One gram of the dried sample is digested with 8N nitric acid and 30% hydrogen peroxide, followed by heating with 25 ml of strong nitric-hydrochloric acid solution to solubilize transition and noble metals. The sample and washings are diluted to 100 ml and a portion of the sample is analyzed for all metals by Inductively Coupled Argon Plasma (ICAP) atomic emission spectrometry.

2.2 Calcium, magnesium, potassium, and sodium are expressed in milligrams per gram (mg/g) of dried sample, whereas concentrations for the other metals are expressed in micrograms per gram (ug/g) of dried sample. Aluminum, iron, and zinc may be expressed either way, depending on the level. Twenty-four metals are routinely reported.

3. SAMPLE HANDLING AND PRESERVATION

3.1 Samples should be collected in clean, polyethylene jars with polypropylene lids, although glass jars with Teflon-lined metal lids may be used.

3.2 Samples should be kept frozen until requested from custody, and refrigerated when not in use.

3.3 No holding times have been established for sediments.

4. SPECIAL SAMPLE TYPES

4.1 Oil samples, and other samples with high organic content, are difficult to analyze with this method. Either they must be treated with several doses of H_2O and concentrated HNO_3 or set aside for separate digestion.

4.2 Samples which are highly colored or have otherwise abnormal appearance may be digested at more than one aliquot size; perhaps, 0.1 or 0.25 g as well as one gram. When the samples are run on the ICAP, the more dilute digests should be run first to determine if levels are high enough to warrant analyzing the more concentrated samples at all.

5. DEFINITION OF TERMS

Refer to "SOP for the Determination of Total Metals in Water"; CRL Method #MET111.

6. APPARATUS

Refer to "SOP for the Determination of Total Metals in Water"; CRL Method #MET111.

7. REAGENTS

Refer to "SOP for the Determination of Total Metals in Water"; CRL Method #MET111.

7.1 Hydrogen peroxide; 30%

7.2 NBS SRM-1645

7.3 U.S. EPA's Municipal Digestion Sludge - Standard #976.

8. INSTRUMENT STANDARDIZATION

Refer to "SOP for the Determination of Total Metals in Water"; CRL Method #MET111.

9. ANALYTICAL PROCEDURE

9.1 Digestion

9.1.1 The samples to be digested together as a unit are arranged in a run sheet with beaker numbers assigned to each sample or quality control audit. Thirty digests is the optimum number of digests which can be attempted, if the grounding of samples is done the day before. All notes regarding the preparation of samples is to be kept on the run sheet which accompanies the samples to the analyst. Both preparer and analyst should initial and date the run sheet. Because the quality control for the run is considered as a unit, the run sheet should be stapled to the QC Report (see Section 11.4).

9.1.2 As was noted earlier in this SOP, Section 6.4, the beakers should be rinsed with hot 1:1 HCl prior to use. This may be done the day before to allow more time for digestion.

9.1.3 A sample dried for the total solids determination (at 105°C overnight to constant weight) is ground with a porcelain mortar and pestle until the entire sample passes through a No. 10 mesh polypropylene sieve. The sieved sample is placed in a two-ounce polypropylene bottle, capped and labeled.

9.1.3.1 One gram of the sample is weighed into a plastic weighing boat. This aliquot is transferred to a 300 ml acid-washed tall form beaker by rinsing the boat with Super-Q water. The beaker is then placed in the hood.

9.1.3.2 A 0.5 ml of 30% hydrogen peroxide and 20 ml of 8N (50%) re-distilled nitric acid are added to the beaker. A ribbed watch glass is placed on the beaker.

9.1.3.3 After heavy foaming subsides, the mixture is swirled to aid in mixing, and then placed on a hot-plate and gently heated short of dryness (1-2 ml) at 95°C.

9.1.3.4 Additional hydrogen peroxide may be required to complete oxidation of organic matter such as humic acid. The same amount of hydrogen peroxide should be added to the blanks as is added to the samples.

9.1.3.5 If the sample is still dark in color, it should have the nitric acid and hydrogen peroxide added to it again. If the color still has not changed after three cycles, it is unlikely that the sample will digest any better. Proceed to 9.1.4.

9.1.4 The beaker is removed from the hot-plate, cooled, and a 25 ml of mixture containing 50 ml of concentrated HCl, 200 ml of concentrated HNO_3, and a 750 ml of deionized water is added. The sample and acid mixture are heated for 15 minutes and cooled.

9.1.5 The contents of the beaker are filtered through a quantitative grade filtered paper, such as Schlichter and Schnell's white label paper, into a clean 100 ml volumetric flask. The empty beaker and watch glass are rinsed with deionized water and a clean rubber policeman (usually contains zinc) or polypropylene spatula is used to remove any deposits. The washings are transferred to the filter and allowed to filter into the volumetric flask. The flask is diluted to the mark, capped, and shaken.

9.1.6 Quality control samples normally included in a run are: blanks - empty beaker plus reagents; duplicates - a separate aliquot of a sample in the run; spikes - a separate aliquot of a sample to which 20 ml of the high level spike solution(s) has been added; lab control standard - a 0.25 g of NBS SRM-1645 River sediment or 1.00 g of the U.S. EPA's Municipal sludge. All of the above are carried through the digestion as if they were samples. The blank, duplicate, and spike should occur at least at the frequency of every 10 samples.

Sediments are often prepared in smaller run sheets because they are not collected as frequently as are water. If as few as 10 samples are on a run sheet, two of each, a blank, duplicate, and spike samples should accompany these samples. With as few as five samples on a run sheet, one of each audit is sufficient. This increased frequency of quality control audits for fewer samples is used to broaden the statistical base for decisions on the validity of the data.

10. CALCULATIONS

Refer to "SOP for the Determination of Total Metals in Water"; CRL Method #MET111.

10.1 Sediments are reported to two significant figures.

10.2 Blanks should be reported with the water detection limit stated.

10.3 The true values of the check samples should be the certified values for NBS SRM-1645 or the U.S. EPA's Municipal sludge. Elements should be limited to those with values already given.

10.3.1 Detection limits should be adjusted with SETVALUE as appropriate to the mass taken for digestion. For example, an element with a detection limit of 5 ug/l in water will be reported to 0.5 ug/g in sediments, if one gram has been digested to 100 ml.

11. QUALITY CONTROL

Refer to "SOP for the Determination of Total Metals in Water"; CRL Method #MET111.

12. ROUTINE MAINTENANCE

Refer to "SOP for the Determination of Total Metals in Water"; CRL Method #MET111.

ICAP SEDIMENT
QC AUDITS

Audit	Frequency	Limits	Corrective Action
AQC	Minimum once per day, following initial standardization	Historical $\bar{X} \pm 2$ Sd on each element	Restandardization. If fresh standard fails, remake standard.
Instrument Blank	Each for approximately 45 min	< 1/2 d.l. each element	Restandardize or check for plugging of nebulizer.
Instrument Check Sample	Each for approximately 45 min	Historical $\bar{X} \pm 3.5\%$ for each element	Restandardize or check for of nebulizer.
Digest Blank	One per 10 samples	< d.l. of element	Up to 8% flags allowable on any one run-sheet; up to four flags allowable on any one audit, such that the average over a six month audit does not exceed 5% flags overall. If three limits are exceeded or if one element of interest is out-of-control, redigest samples.
Digest Duplicate	One per 10 samples	$\pm$ 2 x d.l in digest or $\pm$ 20%	
Digest Spike	One per 10 samples	100 + 15% Recovery if sample < 2 x spike level.	
NBS River Sediment	One per run-sheet (up to 40 samples)	Historical $\bar{X} \pm 20\%$ on known low recovery elements. Historical $\bar{X} \pm 20\%$ for elements with no known value.	

PARAMETER Total Metals* EFFECTIVE DATE January, 1982

METHOD # MET413, MET111 EXPIRATION DATE

METHOD DESCRIPTION Federal Register 44: 233, 200.7

SAMPLE TYPE(S) Sediment, sludges, solids

METHOD REFERENCE HNO_3/H_2O_2 Digestion, ICP analysis

WORKING RANGE See attached Table

DETECTION LIMIT See attached Table UNITS ug/g, mg/g

INSTRUMENT AUDITS

Audit	Frequency	Control Limits	Limit Definition
BLANK	Every 45 minutes	<½ D.L.(See Table 1)	N/A
CHECK Sample (Undigested ICP waste)	Every 45 min	See Table 1	$\bar{X} \pm 2Sd$
STANDARDS	Every run	$\bar{X}$ of 3 burns Cd	N/A
EC Solutions	Every run	>30,000	

METHOD AUDITS

Audit	Frequency	Control Limits	Limit Definition
Blank (Digested)	Once per run or	1x1<D.L.	N/A
Spike (Digested)	every 10	100 ± 10%	$\bar{X} \pm 2Sd$
(Digested) Duplicates	samples.	±D.L. or ±20%	$\bar{X} \pm 2Sd$
Independent Std's	As Requested	"True" ±20%	n<20;preliminary
AQC	Once per run	True ±20%	True ±20%
(NBS SRM-1645 or EMSL Sludge)		See Table 2	$\bar{X} \pm 2Sd$

COMMENTS: Control charts are used for check sample. NOTE: At the 95% level, 8% flags are allowed across all metals/method audits per run; 4 flags are allowed on one method audit across all metals, such that the 6 month total of all flags/all audits/metals does not exceed 5%.

*Al, Ba, Be, B, Ca, Cd, Cr, Co, Cu, Fe, Pb, Li, Mg, M, Mo, Ni, K, Ag, Na, Sr, Sn, V, Y, Zn.

TABLE 1

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Element	Units	Detection Limit	Check Sample Limits	Concentration Range
Al (low)	ug/g	8	3840 - 4547	8 - 2000
(high)	mg/g	-	3.89 - 4.68	2 - 100
Ba	ug/g	0.5	173.9 - 188.01	0.5 - 2000
Be	ug/g	0.1	199.7 - 214.8	0.1 - 2000
B	ug/g	8	289.3 - 317.5	8 - 2000
Ca (low)	mg/g	0.05	62.74 - 72.43	0.05 - 2
(high)	mg/g	-	64.78 - 75.44	2 - 100
Cd	ug/g	0.2	205.4 - 219.66	0.2 - 2000
Cr	ug/g	0.8	650.56 - 699.35	0.8 - 2000
Co	ug/g	0.6	161.34 - 175.06	0.6 - 2000
Cu	ug/g	0.6	665.55 - 704.77	0.6 - 2000
Fe (low)	ug/g	8	12555 - 13336	8 - 2000
(high)	mg/g	-	13 - 14.14	2 - 100
Pb	ug/g	7	376.05 - 471.7	7 - 2000
Li	ug/g	1	116.36 - 147.38	1 - 2000
Mg	mg/g	0.01	4.96 - 5.24	0.01 - 20
Mn	ug/g	0.5	336.84 - 360.37	0.5 - 2000
Mo	ug/g	1	210.21 - 227.43	1 - 2000
Ni	ug/g	1.5	1080.7 - 1167.3	1.5 - 2000
K	mg/g	0.1	6.99 - 8.9	0.1 - 100
Ag	ug/g	0.3	109 - 115	0.3 - 100
Na	mg/g	0.1	15.1 - 18.86	0.1 - 100
Sr	ug/g	1	141.67 - 152.77	1 - 2000
Sn	ug/g	4	190.93 - 223.99	4 - 2000
V	ug/g	0.5	240.48 - 267.4	0.5 - 2000
Y	ug/g	0.5	1070.6 - 1157.7	0.5 - 2000
Zn (low)	ug/g	4	2324.1 - 2630.2	4 - 2000
(high)	mg/g	-	2.47 - 2.87	2 - 100

TABLE 2

CRL METHOD #MET413

EMSL SLUDGE (#MET413)

Dry Sludge Sample (mg/kg)

Parameter	$\bar{X}$	$\bar{X} \pm t_{.95}$ (df)S
Aluminum	4,557.6	2010 - 7110
Beryllium	0.2767	0 - 2.99
Chromium	204.46	115 - 294
Copper	1095.3	831 - 1360
Iron	16155	3810 - 28500
Manganese	204.98	172 - 238
Nickel	198.31	164 - 233
Lead	518.76	305 - 733
Vanadium	13.044	1.7 - 24.4
Zinc	1323.1	1190 - 1450
Cadmium	20.772	2.49 - 39.1
Silver	80.583	0 - 203
Titanium	2121.1	0 - 4860
Arsenic	16.972	0 - 88.9

NBS SRM-1645 LIMITS

Metal	True (ug/g)	Limits
As	(66)	(52.8 - 79.2)
Cd	10.2	8.2 - 12.2
Cr	2.96%	2.34 - 3.55%
Co	(8)	(6.4 - 9.6)
Cu	109	87.2 - 131
Fe	11.3%	9.0 - 12.6%
Pb	714	571 - 857
Mn	785	628 - 942
Ni	45.8	36.6 - 54.9
K	(1.2)	(1.0 - 1.4)
Na	(.55)	(.44 - .66)
V	23.5	18.8 - 28.2
Zn	172.0	168.6 - 175.4

( ) = uncertified value, limits tentative